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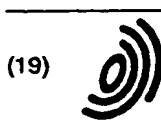
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(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 480 376 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
05.03.1997 Bulletin 1997/10

(51) Int. Cl.⁶: C08F 210/02, C08F 4/69

(21) Application number: 91117138.7

(22) Date of filing: 08.10.1991

(54) Catalyst and process for making bimodal polyolefins

Katalysator und Herstellung von bimodalem Polyolefin

Catalyseur et procédé de préparation de polyoléfines bimodales

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: 09.10.1990 US 594600

(43) Date of publication of application:
15.04.1992 Bulletin 1992/16

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(56) References cited:
EP-A- 0 018 108 DE-A- 2 338 888
US-A- 4 285 834 US-A- 5 032 651

Remarks:

The file contains technical information submitted
after the application was filed and not included in
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Description**Field of the Invention**

5 The present invention relates to olefin polymerization. In another aspect, the present invention relates to catalysts for use in the polymerization of olefins. In still another aspect, the present invention relates to the polymerization of olefins using at least two independent particulate catalysts.

Background of the Invention

10 Various techniques have been employed in the past for the polymerization of polymers and copolymers of olefins. One of the approaches has involved employing catalysts based upon transition metal compounds such as titanium. Another approach has involved the employment of catalysts containing chromium. As a general rule these two types of catalysts produce polyolefins having somewhat different physical characteristics. For some applications, it is desirable 15 to have polyolefins which have a blend of the properties that are produced by the titanium and the chromium catalyst. An example of such polyolefin compositions include those which have been referred to as having bimodal molecular weight distributions. Some techniques for preparing such bimodal polymers have involved the use of multiple reactor arrangements, sometimes loops, sometimes stirred tanks in which different polymerization conditions such as temperature, hydrogen, or comonomer are employed in the different reaction zones. Such multiple reactor schemes, while 20 offering versatility in resin characteristics, can be less efficient than would be desired. The control of the multiple reactor schemes is difficult and reactor size for one resin may by necessity be miss-sized for another. Another technique which has been used to make bimodal polyolefin compositions involves merely blending polyolefin resins having different characteristics; for example, in an extruder to obtain a reasonable homogeneous mixture.

25 In addition, some attempts have been made to combine titanium and chromium on a single catalyst. Examples of such catalyst systems are disclosed in U.S. 3,622,521 and U.S. 4,041,224.

In addition, U.S. 4,285,834 discloses carrying out the polymerization of olefins using a mixture of two independent supported catalysts, one of which contains titanium or vanadium and the other of which contains chromium. While the use of these catalyst mixtures produces some interesting polymers, there is still room for improvement. The improved properties of most bimodal polymers such as those produced by blending result not just from the broad characteristics 30 of the bimodal molecule weight distribution. Instead it is believed that to obtain polymers having the most desirable combination of properties for many applications, it is desirable to obtain a polymer in which the branching is concentrated mainly in the high molecular weight portion of the molecular weight distribution.

An object of the present invention is to provide novel catalyst mixtures.

Another object of the present invention is to provide a process for the polymerization of olefins to produce polymers 35 having a broad molecular weight distribution with the branching concentrated in the high molecular weight portion of the molecular weight distribution.

Another object of the present invention is to provide a mixed catalyst system which can be employed effectively in particle form polymerization of olefins.

Other aspects, objects and advantages of the present invention will become apparent to those skilled in the art having 40 the benefit of this disclosure.

Summary of the Invention

In accordance with the present invention there is provided a method for preparing an ethylene copolymer comprising 45 contacting ethylene and at least one comonomer selected from alpha-olefins containing 3 to 18 carbon atoms in a liquid diluent under particle form polymerization conditions in the presence of a catalyst mixture comprising (1) a particulate chromium-containing catalyst and (2) a particulate titanium-containing catalyst, wherein under the polymerization conditions the chromium-containing catalyst is more effective in incorporating comonomer than the titanium-containing catalyst and produces higher molecular weight polymer than the titanium-containing catalyst.

50 Also in accordance with the present invention, there is provided a catalyst mixture suitable for the polymerization of ethylene. The catalyst mixture comprises (1) a particulate chromium-containing catalyst usually prepared by impregnating a low porosity silica with chromium, activating by contacting with oxygen at a temperature in the range of 427 °C (800°F) to 649 °C (1200°F), and then contacting the activated catalyst with carbon monoxide at a temperature in the range of 260 °C (500°F) to 482 °C (900°F) and (2) a particulate titanium-containing catalyst prepared by reacting a titanium alkoxide with a magnesium dihalide in a suitable liquid to obtain a solution, contacting said solution with a hydrocarbyl aluminum halide to produce a precipitate, contacting said precipitate first with titanium tetrachloride and then with a hydrocarbyl aluminum compound.

55 In an especially preferred embodiment the chromium-containing catalyst and the titanium-containing catalyst are each independently fed to the polymerization zone and the ratio of one catalyst to the other is used to control the melt

index, density, and/or molecular weight distribution of the polymer.

Detailed Description of the Invention

5 The Chromium Containing Catalyst

A large number of patents exists describing various chromium-containing catalysts. Some examples include those U.S. 3,887,494; 3,900,457; 4,053,436; 4,101,722; 4,150,208; 4,151,122; 4,294,724; 4,392,990; 4,405,501; 4,041,224; 3,622,521; 3,798,202, and 2,846,425.

10 The particular chromium catalyst employed can be readily selected by one skilled in the art after having the benefit of this disclosure. Preferably, a chromium catalyst is selected that is not particularly affected by hydrogen or by the small amounts of the cocatalyst that is used with the titanium-containing catalyst. Also, the chromium catalyst should be one which is more effective in incorporating comonomer than the titanium-containing catalyst under the selected polymerization conditions.

15 The amount of chromium in the catalysts can vary over a wide range. Any suitable catalytic amount could be employed. Typically, the chromium-containing catalyst will contain 0.1 to 10 weight percent chromium, more preferably 0.1 to 5 weight percent chromium. As a general rule, catalysts containing about 1 weight percent chromium are preferred. The term weight percent as used in this paragraph refers to weight percent chromium based on the weight of the chromium-containing catalyst.

20 The currently preferred chromium catalysts are low pore volume silica supported catalysts prepared by incorporating chromium on silica and activating in air at a temperature in the range of 427 °C (800°F) to 593°C (1100°F). Preferably the Cr containing silica is then reduced with carbon monoxide at a temperature in the range of 260 °C (500°F) to 482 °C (900°F). Low pore volume catalysts suitable for such an activation and reduction process include catalysts which can be bought from W.R. Grace under the trade designations 9691D, 969MS, 968MS, and 967. Generally it is desirable to employ a catalyst having a porosity of no more than 1.5 cm³, more preferably no more than 1.3 cm³.

The Titanium Catalyst

30 The particular titanium-containing catalyst to be employed can readily be determined by those skilled in the art after having had the benefit of this disclosure.

The titanium catalyst is prepared by contacting a titanium alkoxide and a magnesium dihalide in a suitable liquid to produce a solution. The solution is then contacted with a suitable hydrocarbyl aluminum halide to obtain a solid. The solid, after possibly being contacted with olefin to form prepolymer, is contacted with titanium tetrachloride and then the resulting solid is contacted with a hydrocarbyl aluminum compound prior to the introduction of the solid into a polymerization vessel.

35 Examples of the titanium alkoxides include the titanium tetraalkoxides in which the alkyl groups contain 1 to 10 carbon atoms each. Some specific examples include titanium tetramethoxide, titanium dimethoxide diethoxide, titanium tetraethoxide, titanium tetra-n-butoxide, titanium tetrahexyloxide, titanium tetradecyloxide, and titanium cyclohexyloxide.

The magnesium dihalide is preferably magnesium chloride.

40 The titanium alkoxide and the magnesium dihalide can be combined in any suitable liquid. Examples include substantially anhydrous organic liquids such as n-pentane, n-hexane, n-heptane, methylcyclohexane, toluene and xylenes.

The molar ratio of the transition metal compound to the metal halide can be selected over a relatively broad range. Generally, the molar ratio is within the range of 10 to 1 to 1 to 10, preferably between 3 to 1 to 0.5 to 2; however, more often the molar ratios are within the range of 2 to 1 to 1 to 2.

45 Generally, it is desirable to heat the liquid mixture to obtain a solution. Generally, the components are mixed at a temperature in the range of about 15°C to about 150°C. The mixing could be carried out at atmospheric pressure or at higher pressures.

The time required for mixing the two components is any suitable time which will result in a solution. Generally, this would be a time within the range of 5 minutes to 10 hours. Following the mixing operation, the resulting solution can be filtered to remove any undissolved material or extraneous solid, if desired.

50 The precipitating agent is selected from the group consisting of hydrocarbyl aluminum halides. Preferably the hydrocarbyl aluminum halide is selected from compounds of the formula R_mAlX_{3-m} wherein R is a hydrocarbyl group having 1 to 8 carbons, X is a halogen, and m is a number in the range of 1 to 3. Some specific examples of such compounds include ethylaluminum sesquichloride, diethylaluminum chloride, and ethylaluminum dichloride.

55 The amount of precipitating agent employed can be selected over a relatively broad range depending upon the particular activities desired. Generally, the molar ratio of the transition metal of the titanium-containing component to the precipitating agent is within the range of from 10 to 1 to 1 to 10 and more generally within the range of 2 to 1 to 1 to 3.

In especially preferred embodiments the catalyst contains an amount of prepolymer sufficient to improve the particle size of the catalyst and ultimately the size of the polymer particles produced in a polymerization reaction.

One way of forming prepolymer involves conducting the precipitation in the presence of an aliphatic mono-1-olefin. Another technique involves contacting the precipitated solid with an aliphatic mono-1-olefin under suitable conditions to form prepolymer, either before or after the treatment with titanium tetrachloride. Examples of olefins which can be used for forming prepolymer include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 3-methyl-1-pentene, 1-heptene and 1-octene and mixtures of one or more thereof. The weight of prepolymer based on the total weight of the final prepolymerized catalyst is generally in the range of from about 1 to about 50 weight percent, more preferably 1 to 20 weight percent, and still more preferably 5 to 10 weight percent.

5 The precipitated solid, either with or without prepolymer, is contacted with titanium tetrachloride. The relative ratios of the titanium tetrachloride to the solid can vary over a wide range; however, as a general rule, the weight ratio of the titanium tetrachloride to the prepolymerized or unprepolymerized solid would generally be within the range of 10 to 1 to 10 to 1, more generally 7 to 1 to 1 to 4.

10 Preferably after the precipitated solid is contacted with $TiCl_4$, it is washed several times with a hydrocarbon that acts as a solvent for the $TiCl_4$.

15 The pretreatment of the catalyst with the hydrocarbyl aluminum compound prior to the introduction of the catalyst into the polymerization zone is preferably carried out in a substantially inert liquid, generally a hydrocarbon.

20 The hydrocarbyl aluminum compound that is contacted with the titanium-containing solid catalyst can be selected from generally any of those type of hydrocarbyl aluminum reducing agents that have in the past been used as cocatalysts with such titanium-containing catalysts. The currently preferred organometallic reducing agents are selected from compounds of the formula R_mAlZ_{3-m} wherein R is a hydrocarbyl group having 1 to 8 carbons, Z is a halogen, hydrogen, or hydrocarbyl group having 1 to 8 carbons, and m is a number in the range of 1 to 3. Examples include organoaluminum compounds such as triethylaluminum, trimethylaluminum, diethylaluminum chloride, ethylaluminum dichloride, ethylaluminum sesquichloride, methylaluminum sesquichloride, triisopropylaluminum, dimethylaluminum chloride, tri-decylaluminum, triicosylaluminum, tricyclohexylaluminum, triphenylaluminum, 2-methylpentylidethylaluminum, triisoprenylaluminum, methylaluminum dibromide, ethylaluminum diiodide, isobutylaluminum dichloride, dodecylaluminum dibromide, dimethylaluminum bromide, diisopropylaluminum chloride, methyl-n-propylaluminum bromide, di-n-octylaluminum bromide, diphenylaluminum chloride, dicyclohexylaluminum bromide, methylaluminum sesquibromide and ethylaluminum sesquiodide and mixtures thereof. The currently most preferred organometallic reducing agents are selected from trialkylaluminum compounds, especially triethylaluminum. Preferably each R is an alkyl group containing 1 to 4 carbon atoms.

30 The amount of reducing agent employed in pretreating the titanium-containing catalyst can vary over a wide range. The optimum amount needed for the best overall improvement in the particle form polymerization can be determined by routine experimentation. Generally, excess organometallic reducing agent can be used; however, in such cases it is desirable to subject the resulting product to a number of washes with a suitable solvent, for example a hydrocarbon, to assure that soluble organometallic reducing agent is removed from the catalyst prior to the introduction of the catalyst into the polymerization process. More preferably, the organometallic reducing agent is employed in an amount such that the molar ratio of the reducing agent to titanium in the catalyst would be in the range of 0.01:1 to 10:1, still more preferably 0.02:1 to 3:1. Here again it is generally desirable to subject the resulting catalyst to a wash treatment if the catalyst contains a significant amount of soluble reducing agent.

35 Preferably conditions are employed in all the catalyst preparation steps to minimize the presence of oxygen and water. The contacting can be carried out over a broad range of temperature conditions. Typically, the contacting of the titanium solid and the hydrocarbyl aluminum compound would be conducted at a temperature in the range of 15°C to 150°C, more typically, 20°C to 100°C. After the contacting, the mother liquor is generally decanted and the resulting solids washed several times with suitable liquid solvent such as a hydrocarbon.

40 The resulting pretreated catalyst may if desired be mixed with a particulate diluent such as, for example, silica, silica-alumina, silica-titania, magnesium dichloride, magnesium oxide, polyethylene, polypropylene, and poly(phenylene sulfide), prior to the use of the catalyst in a polymerization process. The weight ratio of the particulate diluent to the catalyst can be varied over a wide range. Typically, the weight ratio of the particulate diluent to the catalyst is generally within the range of 100 to 1 to 1 to 100, or more often in the range of 20 to 1 to 2 to 1. The use of a particulate diluent has been found to be particularly effective in facilitating the controlled charging of the catalyst to the reactor.

45 50 Examples of titanium-containing catalysts which could be pretreated with a hydrocarbyl aluminum compound to yield a titanium-containing catalyst that can be used in combination with the chromium-containing catalyst in accordance with the present invention include prepolymerized titanium catalysts of the type disclosed in U.S. Patent No. 4,325,837.

55 Catalyst Ratios

The ratios of the particulate titanium catalyst to the particulate chromium catalyst can vary over a wide range depending upon the particular properties desired. As a general rule, the weight ratio of the titanium catalyst to the chromium catalyst would be in the range of 99:1 to 1:99, more preferably 80:20 to 20:80. Preferably the catalysts are used

in amounts such that each is responsible for 25 to 75 weight percent of the polymer produced.

Monomers

5 The invention is considered suitable for the copolymerization of ethylene with a wide range of olefins, particularly those aliphatic alpha monoolefins and alpha diolefins having 3 to about 18 carbon atoms. Some examples of such alpha olefins include propylene, butene-1, butadiene, pentene, 3-methylbutene-1, 4-methylpentene-1, hexene-1, octene-1, dodecene-1, octadecene-1, 1,7-octadiene, and mixtures thereof.

10 The amount of alpha olefin comonomer can vary over a wide range. Typically the molar ratio of the comonomer to ethylene would be in the range of about 99:1 to about 1:99, more generally about 25:75 to about 1:99.

The invention is particularly useful for the polymerization of ethylene in combination with small amounts of higher alpha olefins such as butene-1 or hexene-1, generally in amounts of less than 20 weight % based on the weight of the ethylene.

15 Polymerization Conditions

The inventive polymerization process involves carrying out the olefin polymerization under particle form polymerization conditions. This requires the employment of polymerization temperatures in the range of from 60°C to 110°C, more preferably 70°C to 90°C. The reaction can be conducted in a batch reactor or in a suitable continuous reactor. It is generally preferable to carry out the polymerization in an elongated reaction tube which is contacted externally with suitable cooling media to maintain the desired polymerization temperature. A preferred technique uses loop reactor in which the reaction mixture and polymer is circulated within a pipe loop. The time involved for the polymerization will vary depending upon the particular catalyst mixture employed, the temperature, and the desired type of polymer. Typically, when the polymerization is conducted on a commercial scale the residence time is in the range of 1/2 hour to 2 hours.

25 It is generally desirable to carry out the polymerization in the absence of moisture and oxygen. The polymerization is conducted in the presence of a suitable liquid diluent. Examples of such diluents include isobutane, n-butane, n-hexane, isoctane, cyclohexane, methylcyclopentane and dimethylcyclohexane.

30 The polymerization pressures are generally in the range of from about 110 to about 700 psia (1 psia = 6894 Pa), or higher. Typically total Cr and Ti catalyst concentrations would be in the range of 0.001 to 1 weight percent based on the total weight of the polymerization reaction mixture.

In order to obtain polymers with particularly desirable physical properties it is desirable to employ hydrogen during the polymerization period. The amount of hydrogen employed can vary over a wide range depending upon the particular results desired. Typically, the hydrogen would be employed in an amount in the range of 0.5 to 5, more preferably 1.5 to 2.5 mole percent based on the weight of the polymerization diluent.

35 As a general rule it is advantageous to use the mixed catalyst system in combination with a small but effective activating amount of an organometallic cocatalyst. Such organometallic cocatalyst are those of the general type which have in the past been used in activating transition metal containing catalyst systems such as those based upon titanium. Examples of such cocatalyst thus include organo aluminum compounds such as trihydrocarbyl aluminum compounds. Triethylaluminum is a currently favored cocatalyst. The amount of cocatalyst employed can vary over a wide range but its use is limited so that the liquid polymerization diluent does not contain more than 20 ppm of the cocatalyst, more preferably less than 10 ppm. The applicants have observed that, particularly in particle form polymerization the higher levels of cocatalyst tend to deactivate the chromium portion of the catalyst mixture.

40 One of the advantages of the particulate titanium catalyst employed in the present invention is that it can be effective even though the level of cocatalyst such as trialkylaluminum is very low.

45 The polymer is readily recovered from the polymerization mixture by driving off unreacted monomer and liquid diluent. As a general rule, no further removal of impurities is required. In some instances, however, it may be desirable to add a small amount of a catalyst deactivating reagent of the types conventionally employed for deactivating titanium type catalysts.

50 A further understanding of the present invention and its objects and advantages will be provided by the following examples.

55 In the following examples the particulate titanium catalyst was prepared by reacting titanium tetraethoxide with magnesium dichloride to produce a solution. The solution was then contacted with an alkylaluminum halide to obtain a precipitate. Ethylene prepolymer was deposited upon the solid and then the solid was treated with titanium tetrachloride and then washed with a hydrocarbon. A hydrocarbon slurry of the resulting solid was then contacted with triethylaluminum and washed several times with a hydrocarbon to remove soluble triethylaluminum. In order to have a catalyst which would feed well in the equipment being used, the titanium catalyst was admixed with calcined silica.

The chromium catalysts used in the following examples were 951 silica supported chromium catalysts which activated in air at 538 °C (1000°F) and then reduced with carbon monoxide at 371 °C (700°F) prior to use. The chromium catalysts contained about 1 weight percent chromium, based on the total weight of the catalyst.

The experiments set forth in the following examples were carried out using an 87 liter, 15.2 cm diameter pipe loop reactor. Two catalyst mud pipes were employed each with its own catalyst feeder for independent control of the particulate titanium catalyst and the particulate chromium catalyst.

5 Example I

A series of polymerization reactions were carried out using different levels of the titanium and the chromium catalysts to determine the effects of the inventive catalyst mixtures. The polymerizations were conducted at 82 °C (180°F), about 1.5 to about 2 mole percent hydrogen, about 5 to 10 parts per million triethylaluminum cocatalyst, and 1-hexene 10 was used as a comonomer along with the ethylene. The amount of hexene feed was about 15 weight % based on the weight of the ethylene feed. The variations in the polymerization runs and the effects on the resulting polymers are summarized in Table I.

15

Table I

Resins Produced with Varied XPF/Cr Ratios					
Resin	Catalyst, %		HL(MI)	Density	HI
	Ti	Cr			
1	100	0	(42)	0.959	6
2	65	35	81	0.950	23
3	50	50	33	0.948	28
4	40	60	22	0.947	26
5	35	65	5	0.942	31
6	20	80	1	0.940	37
7	0	100	2	0.939	41

30

Table I shows that when the titanium catalyst was used alone, a polymer was obtained which had a melt index of 42 and a density of 0.959. In contrast when all of the catalyst was the particulate chromium-containing catalyst, a polymer was obtained having a high load melt index of 2 and a density of 0.939. The data thus shows that the use of the titanium catalyst alone yields a polymer having an average molecular weight somewhat lower than that of the polymer produced when the catalyst was totally the chromium catalyst. In addition the heterogeneity index (HI) of the polymer formed using only the titanium catalyst was much lower than that of the polymer produced using only the chromium catalyst. This demonstrates that as is known in the art titanium catalysts produces a generally lower molecular weight, narrower molecular weight distribution polymer than do the chromium catalysts. The data reveals further that by using mixtures 35 of the titanium catalyst and the chromium catalyst, in accordance with the present invention, it is possible to both vary the density of the resulting polymer, the molecular weight of the polymer, and the molecular weight distribution. As the chromium component was increased the molecular weight distribution of the polymer was broadened. These polymers were subjected to size exclusion chromatography for a further study of the molecular weight distribution. While the molecular weight distribution of the polymers produced using mixtures of the catalysts remained relatively broad, it was 40 apparent that the peaks of the molecular weight distribution were shifted to lower molecular weight products. This illustrates that both the titanium and the chromium catalysts are contributing, to result in polymers which can be viewed as bimodal, i.e. having molecular weight distribution contributions of both the titanium and the chromium catalysts.

An additional polymerization run was conducted using the same catalyst as was used for Resin 3 in Table I. The reactor conditions, except for temperature, were the same as for the other runs in Table I. This polymerization run differed from that used in making Resin 3 only in that the polymerization was conducted at 88 °C (190°F) rather than 82 °C (180°F). The higher temperature resulted in a slightly narrower molecular weight distribution as evidenced by a heterogeneity index of 24 versus that of 28 for Resin 3. In addition, the higher reactor temperature resulted in a polymer having a somewhat higher high load melt index, specifically a high load melt index of 56 as compared to the high load melt index 33 of Resin 3. This illustrates that by varying the temperature one can make changes in the melt index molecular weight distribution or density of the polymer. In this case the resin produced at 88 °C (190°F) had a density of 0.946 45 as compared to the 0.948 density of Resin 3.

Example II

5 Certain of the polymers from Example I were compounded using a typical bottle resin recipe including antioxidants and the like. Two additional polymerization runs were conducted using a commercial chromium-containing catalyst sold by W. R. Grace as 969 MS. These polymers were also compounded using a typical bottle resin recipe.

10 The polymerization variables and the properties of the polymer compositions are summarized in Table II. Table II further contains the physical properties of a typical bottle composition prepared from a typical commercial scale polymer produced using a chromium catalyst.

Table II

Bottle Resins From Two Catalyst Feeders					
Run	9	10	11	12	Commercial Scale Resin
Catalyst, Ti/Cr	65/35	50/50	969 MS	969 MS	Cr
Reactor Temp., °F	180	180	212	216	--
Reactor Temp., °C	82	82	100	102	
H ₂ , mol%	1.60	1.71	0.22	0.26	--
C ₆ ⁻¹ , wt. % of C ₂ ⁻¹ ⁽¹⁾	15.3	14.8	1.8	1.5	--
TEA, ppm	4.5	4.7	0	0	0
MI, pellet	0.44	0.17	0.43	0.26	0.32
HLM/MI	122	165	86	126	100
Density	0.952	0.950	0.951	0.953	0.952
Productivity (ash) ⁽²⁾	2860	2380	1530	2150	--
Bell ESCR, hrs.	>1000	>1000	112	52	--
PTC Results (105 g. bottle)					
ESCR (Orvusk), hrs.	650	>700	130	80	130
Impact, ft.	9	>12	>12	7	>12
Impact, m	2.7	>3.7	>3.7	2.1	>3.7
Die Swell (bottom layflat)	5.58	5.65	5.40	5.20	5.45

40 (1) C₂⁻¹ = 7-8 mol. %

(2) Residence Time = 75 min.

45 The data in Table II shows that higher titanium to chromium ratios in the inventive mixture produces a higher melt index, higher density polymer. Also the molecular weight distribution as reflected by HLM/MI narrows as the titanium component was increased. Certain properties of the bottle compositions produced using the polymer obtained with the inventive catalyst mixture were comparable to those of the compositions produced using the typical bottle resin which was made in a commercial scale plant. Runs 11 and 12 used the 969 MS catalyst in the pilot plant reactor. It is notable that the bell and bottle ESCR values of the resins produced using the inventive mixed catalyst systems are dramatically higher than those of the resins produced using the MS catalyst.

Example III

55 Another pilot plant polymerization run was carried out using the above-described inventive titanium/chromium mixed particulate catalysts in an attempt to make a polyethylene copolymer comparable to the commercial scale polymers often employed in making plastic pipe. The polymerization conditions are summarized in Table III. For comparison purposes the physical properties of a typical commercial scale pipe resin are included as a control. Both the inventive polymer and the commercial scale polymer were used to make typical natural color pipe compositions.

Table III

Pipe Resin (Natural, Not Black), Two Catalyst Feeders		
Run	13	Control
Catalyst, Ti/Cr	45/55	Cr
Reactor Temp., °F	180	--
Reactor Temp., °C	82	
H ₂ , mol %	1.54	--
C ₆ ⁻¹ , wt. % of C ₂ ⁻¹ ⁽¹⁾	15.2	--
TEA, ppm	4	--
HLMI, pellet	9	11
Density	0.946	0.945
Productivity (ash) ⁽²⁾	2560	--
PTC Results (1" pipe) (1" = 2.54 cm)		
Flex. Mod., Kpsi (D3350)	104	87
Tensile Yield, psi	3200	3150
Tensile Break, psi	3550	5650
Elongation, %	530	880
ESCR, C (milled), hrs.	>2400	>1000

(1) C₂⁻¹ = 7-8 mol. %

(2) Residence Time = 75 min.

The data in Table III shows that the composition produced with the inventive catalyst system has physical properties that are generally comparable to those of the commercial scale pipe resin. It is important to note that the polymer produced with the inventive catalyst composition did exhibit significantly improved environmental stress crack resistance.

Example IV

Another series of runs were conducted using the above-described Ti/Cr catalysts in an attempt to produce polymers which would be suitable for the production of films. The resulting polymers were compounded with the following stabilizers and antioxidants: BHT 0.06 weight percent, DLTDOP 0.03 weight percent, Ultranox 626 0.05 weight percent, and zinc stearate 0.05 weight percent based on the total weight of the polymer. Run 17 differs in that in that case the polymer was also compounded with 0.05 weight percent of FX 9613, a fluoroelastomer. The polymerization variables, the polymer properties, and the composition properties are summarized in Table IV.

Table IV

Film Resins From Two-Catalyst Feeder Studies						
	Run	14	15	16	17 ⁽¹⁾	Control
5	Catalyst, Ti/Cr	50/50	50/50	50/50	36/64	
10	Reactor Temp., °F	190	190	180	180	
15	Reactor Temp., °C	88	88	82	82	
20	H ₂ , mol. %	1.52	1.49	1.71	1.57	
25	C ₆ ⁽²⁾ , wt. % of C ₂ ⁽²⁾	14.9	15.1	14.8	14.2	
30	TEA, ppm ⁽³⁾	5	6	5	4	
35	HL(MI), pellet	17	32	28	3	(0.28)
40	HLMI/MI	170	154	165	--	
45	Density	0.946	0.946	0.950	0.945	0.939
50	Fluff Bulk Density, lbs/ft ³ (1 lbs/ft ³ = 16 kg/m ³)	25.9	25.2	24.4	22.9	
55	Productivity (ash) ⁽⁴⁾	2380	2270	2380	2040	
R&D Film Evaluation (1-mil @ 75 rpm)						
60	Dart Impact, g	121	118	79	260	130
65	Tear, g					
70	MD	21	32	23	41	57
75	TD	483	509	448	157	426

(1) Extruded w/fluoroelastomer

(2) C₂⁽²⁾ = 7-8 mol. %

(3) Based on isobutane feedrate

(4) Polymer residence time = 75 min.

35 The data in Table IV shows that higher polymerization temperatures appear to help the incorporation of the 1-hexene comonomer into the polymer chain as evidenced by the lower density for the resin in Runs 14 and 15 when compared with that of Run 16. The data also reveals that the chromium catalyst appears to incorporate 1-hexene more easily than the titanium catalyst. Accordingly the higher the level of particulate chromium catalyst in the dual catalyst system, the lower the density of the polymers produced. The film properties for the experimentally produced resins were compared with a commercial scale produced film resin composition. The properties of the film compositions were generally comparable.

Claims

45 1. A process for preparing an ethylene copolymer characterized by contacting ethylene and at least one comonomer selected from alpha-olefins containing 3 to 18 carbon atoms in a liquid diluent under particle form polymerization conditions in the presence of a catalyst mixture comprising (1) a particulate chromium-containing catalyst and (2) a particulate titanium-containing catalyst, and an organometallic cocatalyst, wherein said liquid diluent contains no more than 20 parts per million of said cocatalyst, wherein the polymerization is conducted at a temperature in the range of from 60 to 110 °C, wherein said particulate titanium-containing catalyst (2) has been obtained by reacting a titanium alkoxide with a magnesium dihalide in a liquid to obtain a solution, contacting said solution with a hydrocarbyl aluminum halide to produce a precipitate, contacting said precipitate with titanium tetrachloride, and then with a hydrocarbyl aluminum compound, wherein under the polymerization conditions the chromium-containing catalyst is more effective in incorporating the comonomer than the titanium-containing catalyst and produces higher molecular weight polymer than the titanium-containing catalyst.

2. The process of claim 1 wherein the major olefin in terms of molar ratios is ethylene.
3. The process of claim 1 or 2 wherein the chromium catalyst contains from 0.1 to 10 weight percent chromium.
5. The process of any of the preceding claims wherein the olefins that are copolymerized comprise ethylene and 1-hexene.
10. The process of any of the preceding claims wherein the organometallic cocatalyst is an organic aluminum compound, preferably triethylaluminum.
15. The process of any of the preceding claims wherein the polymerization is conducted under such conditions that the branching is concentrated in the high molecular portion of the resulting copolymer; in particular wherein the polymerization is conducted in the presence of hydrogen.
20. The process of any of the preceding claims wherein the weight ratio of the titanium catalyst to the chromium catalyst is in the range of 99:1 to 1:99; preferably 80:20 to 20:80.
25. The process of any of the preceding claims wherein said chromium catalyst and said titanium catalyst are independently fed into the polymerization zone, and the ratio of the chromium catalyst to the titanium catalyst is used to control the melt index density, and/or the molecular weight distribution of the produced copolymer.
30. The process of any of the preceding claims wherein said titanium alkoxide is selected from titanium tetraalkoxides having alkyl groups containing 1 to 10 carbon atoms, said magnesium dihalide is magnesium dichloride, said hydrocarbyl aluminum halide is selected from compounds of the formula R_mAlX_{3-m} wherein R is an alkyl group having 1 to 8 carbon atoms, X is chloride and m is a number in the range of 1 to 3, and said hydrocarbyl aluminum compound is a trialkylaluminum compound in which the alkyl groups contain 1 to 4 carbon atoms.
35. The process of any of the preceding claims wherein said titanium tetraalkoxide is titanium tetraethoxide, said magnesium dihalide is magnesium dichloride, and said hydrocarbylaluminium compound is ethylaluminum sesquichloride, and after contacting the precipitate with titanium tetrachloride, the resulting solid is washed with a hydrocarbon, and then a hydrocarbon slurry of the resulting solid is contacted with triethylaluminum.
40. The process of claim 9 or 10 wherein olefinic prepolymer is deposited on said titanium-containing catalyst.
45. The process of claim 11 wherein the olefinic prepolymer is deposited upon the titanium-containing catalyst before the solid is contacted with the titanium tetrachloride.
50. A catalyst mixture suitable for the polymerization of olefins said mixture comprising (1) a particulate chromium-containing catalyst comprising inorganic oxide and chromium, and (2) a particulate titanium-containing catalyst obtainable by reacting a titanium alkoxide with a magnesium dihalide in a liquid to obtain a solution, contacting said solution with a hydrocarbyl aluminum halide to produce a precipitate, contacting said precipitate with titanium tetrachloride, and then with a hydrocarbyl aluminum compound.
55. The catalyst mixture of claim 13 wherein said titanium alkoxide is selected from titanium tetraalkoxides having alkyl groups containing 1 to 10 carbon atoms, said magnesium dihalide is magnesium dichloride, said hydrocarbyl aluminum halide is selected from compounds of the formula R_mAlX_{3-m} wherein R is an alkyl group having 1 to 8 carbon atoms, X is the chloride and m is a number in the range of 1 to 3, and said hydrocarbyl aluminum compound is a trialkylaluminum compound in which the alkyl groups contain 1 to 4 carbon atoms.
60. The catalyst mixture of claim 14 wherein said titanium tetraalkoxide is titanium tetraethoxide, said magnesium dihalide is magnesium dichloride, and said hydrocarbylaluminium compound is ethylaluminum sesquichloride, and after contacting the precipitate with titanium tetrachloride, the resulting solid is washed with a hydrocarbon, and then a hydrocarbon slurry of the resulting solid is contacted with triethylaluminum.
65. The catalyst mixture of any of claims 13 to 15 wherein olefinic prepolymer is deposited on said titanium-containing catalyst.
70. The catalyst mixture of any of claims 13 to 16 wherein the olefinic prepolymer is deposited upon the titanium-containing catalyst before the solid is contacted with the titanium tetrachloride.

18. An ethylene/1-hexene copolymer produced by the process of any of claims 1 to 12.

Patentansprüche

- 5 1. Verfahren zur Herstellung eines Ethylen-Copolymeren, gekennzeichnet durch Kontaktieren von Ethylen und mindestens einem Comonomeren, das unter α -Olefinen mit 3 bis 18 Kohlenstoffatomen ausgewählt ist, in einem flüssigen Verdünnungsmittel unter Teilchenform-Polymerisationsbedingungen in Gegenwart eines Katalysatorgemisches, das (1) einen teilchenförmigen chromhaltigen Katalysator und (2) einen teilchenförmigen titanhaltigen Katalysator enthält, und eines Organometall-Cokatalysators,
 - 10 wobei das flüssige Verdünnungsmittel nicht mehr als 20 ppm des Cokatalysators enthält,
 - wobei die Polymerisation bei einer Temperatur im Bereich von 60 bis 110°C durchgeführt wird,
 - wobei der teilchenförmige titanhaltige Katalysator (2) durch Umsetzen eines Titanalkoxids mit einem Magnesiumdihalogenid in einer Flüssigkeit unter Bildung einer Lösung, durch Kontaktieren der Lösung mit einem Hydrocarbylaluminiumhalogenid unter Bildung eines Niederschlags und durch Kontaktieren des Niederschlags mit Titanetrachlorid und anschließend mit einer Hydrocarbylaluminiumverbindung hergestellt worden ist,
 - 15 wobei unter den Polymerisationsbedingungen der chromhaltige Katalysator im Vergleich zum titanhaltigen Katalysator eine wirksamere Einverleibung des Comonomeren bewirkt und im Vergleich zum titanhaltigen Katalysator ein höhermolekulares Polymeres ergibt.
- 20 2. Verfahren nach Anspruch 1, wobei es sich bei dem Hauptolefin, bezogen auf das Molverhältnis, um Ethylen handelt.
3. Verfahren nach Anspruch 1 oder 2, wobei der Chromkatalysator 0,1 bis 10 Gew.-% Chrom enthält.
- 25 4. Verfahren nach einem der vorstehenden Ansprüche, wobei die Olefine, die copolymerisiert werden, Ethylen und 1-Hexen umfassen.
5. Verfahren nach einem der vorstehenden Ansprüche, wobei es sich beim organometallischen Cokatalysator um eine organische Aluminiumverbindung und vorzugsweise um Triethylaluminium handelt.
- 30 6. Verfahren nach einem der vorstehenden Ansprüche, wobei die Polymerisation unter solchen Bedingungen durchgeführt wird, daß sich die Verzweigung im hochmolekularen Bereich des erhaltenen Copolymeren konzentriert, wobei insbesondere die Polymerisation in Gegenwart von Wasserstoff durchgeführt wird.
7. Verfahren nach einem der vorstehenden Ansprüche, wobei das Gewichtsverhältnis des Titankatalysators zum Chromkatalysator im Bereich von 99:1 bis 1:99 und vorzugsweise von 80:20 bis 20:80 liegt.
- 35 8. Verfahren nach einem der vorstehenden Ansprüche, wobei der Chromkatalysator und der Titankatalysator unabhängig voneinander in die Polymerisationszone eingespeist werden, und das Verhältnis des Chromkatalysators zum Titankatalysator dazu herangezogen wird, den Schmelzindex, die Dichte und/oder die Molekulargewichtsverteilung des gebildeten Copolymeren zu steuern.
9. Verfahren nach einem der vorstehenden Ansprüche, wobei das Titanalkoxid unter Titantetraalkoxiden mit Alkyresten mit 1 bis 10 Kohlenstoffatomen ausgewählt wird, wobei es sich beim Magnesiumdihalogenid um Magnesiumdichlorid handelt, wobei das Hydrocarbylaluminiumhalogenid unter Verbindungen der Formel R_mAlX_{3-m} ausgewählt wird, wobei R einen Alkylrest mit 1 bis 8 Kohlenstoffatomen bedeutet, X Chlorid bedeutet und m eine Zahl im Bereich von 1 bis 3 ist, und wobei es sich bei der Hydrocarbylaluminiumverbindung um eine Trialkylaluminiumverbindung handelt, bei der die Alkylreste 1 bis 4 Kohlenstoffatome enthalten.
- 45 10. Verfahren nach einem der vorstehenden Ansprüche, wobei es sich beim Titanalkoxid um Titanetraethoxid handelt, wobei es sich beim Magnesiumdihalogenid um Magnesiumdichlorid handelt und wobei es sich bei der Hydrocarbylaluminiumverbindung um Ethylaluminiumsesquichlorid handelt und wobei nach dem Kontaktieren des Niederschlags mit Titanetrachlorid der erhaltene Feststoff mit einem Kohlenwasserstoff gewaschen wird, und anschließend eine Kohlenwasserstoffaufschämmung des erhaltenen Feststoffs mit Triethylaluminium kontaktiert wird.
- 55 11. Verfahren nach Anspruch 9 oder 10, wobei olefinisches Präpolymeres auf dem titanhaltigen Katalysator abgeschieden wird.

12. Verfahren nach Anspruch 11, wobei das olefinische Präpolymere auf dem titanhaltigen Katalysator abgeschieden wird, bevor der Feststoff mit dem Titanetrachlorid kontaktiert wird.

5 13. Zur Polymerisation von Olefinen geeignetes Katalysatorgemisch, enthaltend (1) einen teilchenförmigen chromhaltigen Katalysator, der anorganisches Oxid und Chrom enthält, und (2) einen teilchenförmigen titanhaltigen Katalysator, der erhältlich ist durch Umsetzen eines Titanalkoxids mit einem Magnesiumdihalogenid in einer Flüssigkeit unter Bildung einer Lösung, durch Kontaktieren der Lösung mit einem Hydrocarbylaluminiumhalogenid unter Bildung eines Niederschlags und durch Kontaktieren des Niederschlags mit Titanetrachlorid und anschließend mit einer Hydrocarbylaluminiumverbindung.

10 14. Katalysatorgemisch nach Anspruch 13, wobei das Titanalkoxid unter Titanetraalkoxiden mit Alkylresten mit 1 bis 10 Kohlenstoffatomen ausgewählt wird, wobei es sich beim Magnesiumdihalogenid um Magnesiumdichlorid handelt, wobei das Hydrocarbylaluminiumnalogenid unter Verbindungen der Formel R_mAlX_{3-m} ausgewählt wird, wobei R einen Alkylrest mit 1 bis 8 Kohlenstoffatomen bedeutet, X Chlorid bedeutet und m eine Zahl im Bereich von 1 bis 15 3 ist, und wobei es sich bei der Hydrocarbylaluminiumverbindung um eine Trialkylaluminiumverbindung handelt, bei der die Alkylreste 1 bis 4 Kohlenstoffatome enthalten.

20 15. Katalysatorgemisch nach Anspruch 14, wobei es sich beim Titanetraalkoxid um Titanetraethoxid handelt, wobei es sich beim Magnesiumdihalogenid um Magnesiumdichlorid handelt und wobei es sich bei der Hydrocarbylaluminiumverbindung um Ethylaluminiumsesquichlorid handelt und wobei nach dem Kontaktieren des Niederschlags mit Titanetrachlorid der erhaltene Feststoff mit einem Kohlenwasserstoff gewaschen wird, und anschließend eine Kohlenwasserstoffsäufschämmung des erhaltenen Feststoffs mit Triethylaluminium kontaktiert wird.

25 16. Katalysatorgemisch nach einem der Ansprüche 13 bis 15, wobei olefinisches Präpolymeres auf dem titanhaltigen Katalysator abgeschieden worden ist.

17. Katalysatorgemisch nach einem der Ansprüche 13 bis 16, wobei das olefinische Präpolymere auf dem titanhaltigen Katalysator vor dem Kontaktieren des Feststoffs mit dem Titanetrachlorid abgeschieden worden ist.

30 18. Ein Ethylen/1-Hexen-Copolymeres, gebildet durch das Verfahren von einem der Ansprüche 1 bis 12.

Revendications

1. Un procédé pour la préparation d'un copolymère d'éthylène caractérisé par la mise en contact d'éthylène et d'au moins un comonomère choisi parmi les α -oléfines renfermant de 3 à 18 atomes de carbone dans un diluant liquide 35 sous des conditions de polymérisation sous forme particulaire en présence d'un mélange de catalyseur comprenant (1) un catalyseur contenant du chrome particulaire et (2) un catalyseur contenant du titane particulaire et un cocatalyseur organométallique, dans lequel ledit diluant liquide ne renferme pas plus de 20 parties par million dudit cocatalyseur, 40 dans lequel la polymérisation est mise en œuvre à une température comprise dans la gamme de 60 à 110°C, dans lequel ledit catalyseur contenant du titane particulaire (2) a été obtenu en faisant réagir un alcoxyde de titane avec un dihalogénure de magnésium dans un liquide pour obtenir une solution, en mettant en contact ladite 45 solution avec un halogénure d'hydrocarbyl-aluminium pour produire un précipité, en mettant en contact ledit précipité avec du tétrachlorure de titane et ensuite avec un composé d'hydrocarbyl-aluminium, dans lequel sous les conditions de polymérisation le catalyseur contenant du chrome est plus efficace en incorporant le comonomère plutôt que le catalyseur contenant du titane et produit un polymère de poids moléculaire supérieur que le catalyseur contenant du titane.

50 2. Le procédé selon la revendication 1, dans lequel l'oléfine principale en terme de rapports molaires est l'éthylène.

3. Le procédé selon la revendication 1 ou 2, dans lequel le catalyseur de chrome renferme de 0,1 à 10 % en poids de chrome.

55 4. Le procédé selon l'une quelconque des revendications précédentes, dans lequel les oléfines qui sont copolymérisées renferment de l'éthylène et du 1-hexène.

5. Le procédé selon l'une quelconque des revendications précédentes, dans lequel le cocatalyseur organométallique est un composé d'aluminium organique, de préférence, du triéthylaluminium.

6. Le procédé selon l'une quelconque des revendications précédentes, dans lequel la polymérisation est mise en oeuvre sous des conditions telles que la ramification est concentrée dans la partie de poids moléculaire élevée du copolymère résultant, en particulier dans lequel la polymérisation est mise en oeuvre en présence d'hydrogène.

5 7. Le procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport pondéral du catalyseur de titane au catalyseur de chrome se situe dans la gamme de 99:1 à 1:99, de préférence de 80:20 à 20:80.

8. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit catalyseur de chrome et ledit catalyseur de titane son alimentés indépendamment dans la zone de polymérisation et le rapport du catalyseur de chrome au catalyseur de titane est utilisé pour contrôler l'indice à l'état fondu, la densité et/ou la répartition de poids moléculaire du copolymère produit.

10 9. Le procédé selon l'une quelconque des revendications précédentes, dans lequel l'alcoxyde de titane est choisi parmi les tétraalcoxydes de titane ayant des groupes alkyle contenant de 1 à 10 atomes de carbone, le dihalogénure de magnésium est le dichlorure de magnésium, ledit halogénure d'hydrocarbyl-aluminium est choisi parmi les composés de formule R_mAlX_{3-m} où R est un groupe alkyle ayant de 1 à 8 atomes de carbone, X est un chlorure et m est un nombre compris dans la gamme de 1 à 3 et ledit composé d'hydrocarbyl-aluminium est un composé de trialkylaluminium dans lequel les groupes alkyle renferment de 1 à 4 atomes de carbone.

15 20 10. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit tétraalcoxyde de titane est le tétraéthoxyde de titane, ledit dihalogénure de magnésium est le dichlorure de magnésium, et ledit composé hydrocarbyl-aluminium est le sesquichlorure d'éthylaluminium, et après la mise en contact du précipité avec le tétrachlorure de titane, le solide résultant est lavé avec un hydrocarbure et ensuite une bouillie hydrocarbonée du solide résultant est mise en contact avec du triéthylaluminium.

25 11. Le procédé selon la revendication 9 ou 10, dans lequel un prépolymère oléfinique est déposé sur ledit catalyseur contenant du titane.

12. Le procédé selon la revendication 11, dans lequel le prépolymère oléfinique est déposé sur le catalyseur contenant du titane avant que le solide soit mis en contact avec le tétrachlorure de titane.

30 35 13. Un mélange de catalyseur approprié pour la polymérisation d'oléfines, ledit mélange comprenant (1) un catalyseur contenant du chrome particulier comprenant un oxyde non organique et du chrome et (2) un catalyseur contenant du titane particulier apte à être obtenu en faisant réagir un alcoxyde de titane avec un dihalogénure de magnésium dans un liquide pour obtenir une solution, en mettant en contact ladite solution avec un halogénure d'hydrocarbyl-aluminium pour produire un précipité, en mettant en contact ledit précipité avec du tétrachlorure de titane et ensuite avec un composé d'hydrocarbyl-aluminium.

40 14. Le mélange de catalyseur selon la revendication 13, dans lequel ledit alcoxyde de titane est choisi parmi les tétraalcoxydes de titane ayant des groupes alkyle contenant de 1 à 10 atomes de carbone, ledit dihalogénure de magnésium est le dichlorure de magnésium, ledit halogénure d'hydrocarbyl-aluminium est choisi parmi les composés de formule R_mAlX_{3-m} où R est un groupe alkyle ayant de 1 à 8 atomes de carbone, X est le chlorure et m est un nombre compris dans la gamme de 1 à 3 et ledit composé d'hydrocarbyl-aluminium est un composé de trialkylaluminium dans lequel les groupes alkyle renferment de 1 à 4 atomes de carbone.

45 15. Le mélange de catalyseur selon la revendication 14, dans lequel ledit tétraalcoxyde de titane est le tétraéthoxyde de titane, ledit dihalogénure de magnésium est du dichlorure de magnésium et ledit composé d'hydrocarbyl-aluminium est du sesquichlorure d'éthylaluminium et après la mise en contact du précipité avec du tétrachlorure de titane, le solide résultant est lavé avec un hydrocarbure et ensuite une bouillie hydrocarbonée du solide résultant est mise en contact avec du triéthylaluminium.

50 16. Le mélange de catalyseur selon l'une quelconque des revendications 13 à 13, dans lequel un prépolymère oléfinique est déposé sur ledit catalyseur contenant du titane.

55 17. Le mélange de catalyseur selon l'une quelconque des revendications 13 à 16, dans lequel le prépolymère oléfinique est déposé sur le catalyseur contenant du titane avant que le solide soit mis en contact avec le tétrachlorure de titane.

18. Un copolymère éthylène/1-hexène produit par le procédé selon l'une quelconque des revendications 1 à 12.